REPORT ON MICROANALYTICAL DETERMINATION OF NITROGEN

(FOR N-N, NO AND NO_2 LINKAGES)

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The hydriodic reduction method for reducing compounds containing N–N and N–O groups before determining the nitrogen by the Kjeldahl method, proposed in the 1950 report on microchemical methods, was studied again this year. Two samples which contained these nitrogen linkages, acetone-2,-4-dinitrophenyl hydrazone and benzotriazole, were sent to those collaborators who had expressed a willingness to study the method further. The following procedure, a modification of the Friedrich method, was used in this study:

Weigh in a charging tube about 10 mg of sample and transfer to a 30 ml Kjeldahl digestion flask. Add 1 ml of hydriodic acid, sp. g. 1.70 (57%), and add boiling chips

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to prevent bumping; gently reflux the mixture for 45 min. Cool, add 5 ml of water, and 2 ml of sulfuric acid; heat the mixture at *full heat* until the water is removed and the sulfuric acid *refluxes* up in the neck of the flask. Cool, add 2 ml, H_2O, and repeat the distillation. If iodine vapors are not removed completely, repeat the distillation step until no more iodine remains.

Cool, add 0.65 g of K_2SO_4, 40 mg of HgO, and 1 ml of H_2O; digest for 1 hour with the *sulfuric acid* refluxing 4–8 cm into the neck of the flask. (For the sample containing the ring nitrogen, add 1.3 g of K_2SO_4 and digest for 4 hours.)

Continue the determination beginning with "Cool, add minimum of distilled water . . . " in the first action procedure (*Methods of Analysis*, 7th Ed., 37.4).

In 1949 it was found that a hydriodic acid pretreatment produces low and erratic results. Because of this, the Friedrich (hydriodic acid) method was deleted from the *Book of Methods*. The modification used this year differs from that studied in 1949 in three respects. In this year's procedure, the potassium sulfate for the Kjeldahl digestion was not added until *all* HI was removed, only one-half as much potassium sulfate (0.65 g) was added, and more emphasis was placed on removing completely all HI before beginning the digestion with potassium sulfate and mercuric oxide catalyst.

Twelve analysts reported results for sample No. 1, acetone-2, 4-dinitrophenyl hydrazone, and ten reported for sample No. 2, benzotriazole. Theoretical nitrogen percentages for the two pure compounds are 23.62 and 35.28%, respectively. Table 1 shows the results. In this table, n is the

TABLE 1.—*Results of the collaborative study of the determination of nitrogen in compounds having N-N and N-O linkages using the Kjeldahl method with HI pretreatment*

COLLABORATOR NO.	ACETONE-2, 4-DINITROPHENYL HYDRAZONE			BENZOTRIAZOLE		
	n	$\bar{X}$	s	n	$\bar{X}$	s
0	8	23.27	0.075	8	34.27	0.099
8	3	23.50	0.076	4	34.19	0.168
15	5	22.63	0.082	5	32.16	0.320
23	3	23.22	0.066	4	34.06	0.119
24	5	23.50	0.111	5	32.46	0.752
29	3	23.50	0.329	3	33.74	0.872
35	6	21.91	0.062			
37	4	23.45	0.363	6	33.34	0.642
59	2	23.73	1.017	2	28.95	0.092
1	5	23.18	0.191			
22	2	22.75	0.065	2	33.87	0.190
19	10	23.23	0.338			
36				8	31.89	0.435
$\bar{\bar{X}}$		23.16	(0.225)		32.90	(0.369)
$s_{\bar{x}}$		0.334			1.63	
Theoretical Value		23.62%			35.28%	

number of determinations reported, $\overline{X}$ is the analyst's mean value, and s is the standard deviation of his values. $\overline{\overline{X}}$ is the mean of the analyst's mean, $\overline{X}$'s. For sample No. 1 this was 23.16%, as opposed to a theoretical value of 23.62%. Six of the twelve analyst's means were within 0.2% of the true value; all the other six values were lower than the theoretical value by more than 0.2%. The standard deviation of the mean, $s_{\bar{x}}$, was 0.334, whereas the mean of the individual standard deviations was 0.225, showing that on the average, the results of each analyst were more precise than were the averages of all analysts.

The corresponding values for sample No. 2, which contains three nitrogens linked together in a ring compound were also determined. The value for the grand mean, $\overline{\overline{X}}$, was 32.90%, as compared with a theoretical value of 35.28%. The standard deviation of the means, $s_{\bar{x}}$, was 1.63, and the mean of the individual s values was 0.369. Collaborator 19, not listed in Table 1, reported no values for Sample No. 2 but said that his results ranged from 16.03 to 24.42%. These data show that the nitrogen values obtained for this sample by the proposed method were much poorer than those for sample No. 1.

In the previous study of this method of pretreatment (1), methyl orange was the test sample, and a mean value of 11.02% nitrogen was obtained as compared with a value of 11.50% by the Dumas method. The standard deviation of all the values reported was 0.496. Although the nitrogen values for methyl orange deviated more from the theoretical value than did those obtained this year for sample No. 1, they were closer to the theoretical value than those for sample No. 2.

Although the results have neither a $\overline{\overline{X}}$ value sufficiently near to the theoretical value for nitrogen nor a sufficiently low standard deviation of the mean values to indicate good precision among analysts, they do indicate that the differences in accuracy and precision were more closely related to the nature of the compounds analyzed than to the methods used. The results obtained for acetone-2, 4-dinitrophenyl hydrazone, which has one N–N linkage and two NO_2 groups, were better than those for benzotriazole, which has the N–N–N linkage, and for methyl orange, which has one N–N linkage and one amine group. This indicates that the method may be more satisfactory for compounds containing N–O linkages than those containing N–N linkages.

RECOMMENDATIONS*

The referees recommend that the method used in this year's study be tested on compounds containing only NO and NO_2 groups and that a search be made for another modification of the Kjeldahl method or pretreatment suitable for determining nitrogen in compounds containing the N–N linkage.

* For report of Subcommittee C and action of the Association, see *This Journal*, 35, 53 (1952).

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LITERATURE CITED

(1) Willits, C. O., and Ogg, C. L., *This Journal*, **32**, 561 (1949).